

**Claims:**

1. A method of forming a film on a substrate, comprising:  
positioning the substrate within a process chamber; and  
forming a ruthenium layer on at least a portion of the substrate by sequentially chemisorbing monolayers of a ruthenium-containing compound and a reducing gas.
2. The method of claim 1, wherein the process chamber is purged with a purge gas following chemisorption of each monolayer.
3. The method of claim 2, wherein the ruthenium-containing compound is selected from the group consisting of:  
tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium;  
bis(2,4-dimethylpentadienyl)ruthenium;  
dicarbonyl pentadienyl ruthenium; ruthenium acetyl acetonate;  
(2,4-dimethylpentadienyl)ruthenium(cyclopentadienyl);  
bis(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium(1,5-cyclooctadiene);  
(2,4-dimethylpentadienyl)ruthenium(methylcyclopentadienyl);  
(1,5-cyclooctadiene)ruthenium(cyclopentadienyl);  
(1,5-cyclooctadiene)ruthenium(methylcyclopentadienyl);  
(1,5-cyclooctadiene)ruthenium(ethylcyclopentadienyl);  
(2,4-dimethylpentadienyl)ruthenium(ethylcyclopentadienyl);  
(2,4-dimethylpentadienyl)ruthenium(isopropylcyclopentadienyl);  
bis(N,N-dimethyl 1,3-tetramethyl diiminato)ruthenium(1,5-cyclooctadiene);  
bis(N,N-dimethyl 1,3-dimethyl diiminato)ruthenium(1,5-cyclooctadiene);  
bis(allyl)ruthenium(1,5-cyclooctadiene), ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)ruthenium(1,3-cyclohexadiene);  
bis(1,1-dimethyl-2-aminoethoxylato)ruthenium(1,5-cyclooctadiene);  
bis(1,1-dimethyl-2-aminoethylaminato)ruthenium(1,5-cyclooctadiene);  
and combinations thereof.

PATENT

Attorney Docket No.: AMAT/5975.P1/CPI/COPPER/BG

Express Mail No.: EV351031212US

4. The method of claim 3, wherein the reducing gas comprises one or more gases selected from the group consisting of hydrogen, ammonia, silane, disilane, dimethylsilane, methylsilane, ethylsilane, chlorosilane, dichlorosilane, hexachlorodisilane, borane, diborane, triborane, tetraborane, pentaborane, triethylborane, and combinations thereof.
5. The method of claim 4, wherein forming the ruthenium layer is performed at a temperature in a range from about 200°C to about 400°C.
6. The method of claim 4, wherein forming the ruthenium layer is performed at a pressure in a range from about 0.1 Torr to about 80 Torr.
7. The method of claim 2, wherein the purge gas is selected from the group consisting of helium, argon, hydrogen, nitrogen, and combinations thereof.
8. The method of claim 6, wherein the ruthenium-containing compound is pulsed into the process chamber in a range from about 0.05 seconds to about 1.5 seconds.
9. The method of claim 8, wherein the reducing gas is pulsed into the process chamber in a range from about 0.1 seconds to about 2 seconds.
10. The method of claim 7, wherein the purge gas is pulsed into the process chamber in a range from about 0.07 seconds to about 1 second.
11. The method of claim 4, wherein the ruthenium layer has a thickness in a range from about 10 Å to about 100 Å.
12. The method of claim 4, wherein the ruthenium-containing compound passes through a gas delivery apparatus and is injected into the process chamber.

PATENT

Attorney Docket No.: AMAT/5975.P1/CPI/COPPER/BG

Express Mail No.: EV351031212US

13. The method of claim 12, wherein the ruthenium-containing compound is delivered normal to the substrate with respect to the substrate.

14. A method of forming a ruthenium layer on a substrate for use in integrated circuit fabrication, comprising:

positioning the substrate within a process chamber, wherein the process chamber is in fluid communication with a gas delivery system;

delivering a ruthenium-containing compound from the gas delivery system to the process chamber;

chemisorbing a ruthenium-containing layer on the substrate;

delivering a reducing gas from the gas delivery system to the process chamber;

and

reacting the reducing gas with the ruthenium-containing layer to form the ruthenium layer on the substrate.

15. The method of claim 14, wherein the chamber is purged with a purge gas preceding and following the delivery of the reducing gas.

16. The method of claim 15, wherein the ruthenium-containing compound is selected from the group consisting of:

tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium;

bis(2,4-dimethylpentadienyl)ruthenium;

dicarbonyl pentadienyl ruthenium; ruthenium acetyl acetate;

(2,4-dimethylpentadienyl)ruthenium(cyclopentadienyl);

bis(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium(1,5-cyclooctadiene);

(2,4-dimethylpentadienyl)ruthenium(methylcyclopentadienyl);

(1,5-cyclooctadiene)ruthenium(cyclopentadienyl);

(1,5-cyclooctadiene)ruthenium(methylcyclopentadienyl);

(1,5-cyclooctadiene)ruthenium(ethylcyclopentadienyl);

(2,4-dimethylpentadienyl)ruthenium(ethylcyclopentadienyl);

(2,4-dimethylpentadienyl)ruthenium(isopropylcyclopentadienyl);

PATENT

Attorney Docket No.: AMAT/5975.P1/CPI/COPPER/BG

Express Mail No.: EV351031212US

bis(N,N-dimethyl 1,3-tetramethyl diiminato)ruthenium(1,5-cyclooctadiene);  
bis(N,N-dimethyl 1,3-dimethyl diiminato)ruthenium(1,5-cyclooctadiene);  
bis(allyl)ruthenium(1,5-cyclooctadiene), ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)ruthenium(1,3-cyclohexadiene);  
bis(1,1-dimethyl-2-aminoethoxylato)ruthenium(1,5-cyclooctadiene);  
bis(1,1-dimethyl-2-aminoethylaminato)ruthenium(1,5-cyclooctadiene);  
and combinations thereof.

17. The method of claim 16, wherein the reducing gas comprises one or more gases selected from the group consisting of hydrogen, ammonia, silane, disilane, dimethylsilane, methylsilane, ethylsilane, chlorosilane, dichlorosilane, hexachlorodisilane, borane, diborane, triborane, tetraborane, pentaborane, triethylborane, and combinations thereof.

18. The method of claim 17, wherein forming the ruthenium layer is performed at a temperature in a range from about 200°C to about 400°C.

19. The method of claim 17, wherein forming the ruthenium layer is performed at a pressure in a range from about 0.1 Torr to about 80 Torr.

20. The method of claim 15, wherein the purge gas is selected from the group consisting of helium, argon, hydrogen, nitrogen, and combinations thereof.

21. The method of claim 19, wherein the ruthenium-containing compound is pulsed into the process chamber in a range from about 0.05 seconds to about 1.5 seconds.

22. The method of claim 21, wherein the reducing gas is pulsed into the process chamber in a range from about 0.1 seconds to about 2 seconds.

23. The method of claim 20, wherein the purge gas is pulsed into the process chamber in a range from about 0.07 seconds to about 1 second.

PATENT

Attorney Docket No.: AMAT/5975.P1/CPI/COPPER/BG

Express Mail No.: EV351031212US

24. The method of claim 17, wherein the ruthenium layer has a thickness in a range from about 10 Å to about 100 Å.
25. The method of claim 17, wherein the ruthenium-containing compound passes through a gas delivery apparatus and is injected into the process chamber.
26. The method of claim 25, wherein the ruthenium-containing compound is delivered normal to the substrate with respect to the substrate.
27. A method for forming a layer comprising ruthenium on a substrate surface within a process chamber, sequentially comprising:
- a) exposing the substrate surface to a ruthenium-containing compound to form a ruthenium-containing layer on the substrate surface;
  - b) purging the process chamber with a purge gas;
  - c) reacting a reducing gas with the ruthenium-containing layer; and
  - d) purging the process chamber with the purge gas.
28. The method of claim 27, wherein the layer is formed by an ALD process cycle including repeating steps a-d.
29. The method of claim 28, wherein the ruthenium-containing compound is selected from the group consisting of:
- tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium;
  - bis(2,4-dimethylpentadienyl)ruthenium;
  - dicarbonyl pentadienyl ruthenium; ruthenium acetyl acetate;
  - (2,4-dimethylpentadienyl)ruthenium(cyclopentadienyl);
  - bis(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium(1,5-cyclooctadiene);
  - (2,4-dimethylpentadienyl)ruthenium(methylcyclopentadienyl);
  - (1,5-cyclooctadiene)ruthenium(cyclopentadienyl);
  - (1,5-cyclooctadiene)ruthenium(methylcyclopentadienyl);
  - (1,5-cyclooctadiene)ruthenium(ethylcyclopentadienyl);

(2,4-dimethylpentadienyl)ruthenium(ethylcyclopentadienyl);  
(2,4-dimethylpentadienyl)ruthenium(isopropylcyclopentadienyl);  
bis(N,N-dimethyl 1,3-tetramethyl diiminato)ruthenium(1,5-cyclooctadiene);  
bis(N,N-dimethyl 1,3-dimethyl diiminato)ruthenium(1,5-cyclooctadiene);  
bis(allyl)ruthenium(1,5-cyclooctadiene), ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)ruthenium(1,3-cyclohexadiene);  
bis(1,1-dimethyl-2-aminoethoxylato)ruthenium(1,5-cyclooctadiene);  
bis(1,1-dimethyl-2-aminoethylaminato)ruthenium(1,5-cyclooctadiene);  
and combinations thereof.

30. The method of claim 29, wherein the reducing gas comprises one or more gases selected from the group consisting of hydrogen, ammonia, silane, disilane, dimethylsilane, methylsilane, ethylsilane, chlorosilane, dichlorosilane, hexachlorodisilane, borane, diborane, triborane, tetraborane, pentaborane, triethylborane, and combinations thereof.

31. The method of claim 30, wherein forming the ruthenium layer is performed at a temperature in a range from about 200°C to about 400°C.

32. The method of claim 30, wherein forming the ruthenium layer is performed at a pressure in a range from about 0.1 Torr to about 80 Torr.

33. The method of claim 28, wherein the purge gas is selected from the group consisting of helium, argon, hydrogen, nitrogen, and combinations thereof.

34. The method of claim 32, wherein the ruthenium-containing compound is pulsed into the process chamber in a range from about 0.05 seconds to about 1.5 seconds.

35. The method of claim 34, wherein the reducing gas is pulsed into the process chamber in a range from about 0.1 seconds to about 2 seconds.

PATENT

Attorney Docket No.: AMAT/5975.P1/CPI/COPPER/BG

Express Mail No.: EV351031212US

36. The method of claim 33, wherein the purge gas is pulsed into the process chamber in a range from about 0.07 seconds to about 1 second.

37. The method of claim 30, wherein repeating steps a-d forms the ruthenium layer with a thickness in a range from about 10 Å to about 100 Å.

38. The method of claim 30, wherein the ruthenium-containing compound passes through a gas delivery apparatus and is injected into the process chamber.

39. The method of claim 38, wherein the ruthenium-containing compound is delivered normal to the substrate surface with respect to the substrate surface.

40. A method of forming a ruthenium layer on a substrate, comprising:  
positioning the substrate within a process chamber, wherein the process chamber comprises:

- a substrate support having the substrate;

- a chamber lid comprising a passageway at a central portion of the chamber lid and comprising a bottom surface extending from the passageway to a peripheral portion of the chamber lid, the bottom surface shaped and sized to substantially cover the substrate;

- one or more valves coupled to the passageway;

- one or more gas sources coupled to each valve; and

- a reaction zone defined between the chamber lid and the substrate, the reaction zone comprising a small volume; and

- forming the ruthenium layer on at least a portion of the substrate by sequentially chemisorbing monolayers of a ruthenium-containing compound and a reducing gas.

41. The method of claim 40, wherein the process chamber is purged with a purge gas following chemisorption of each monolayer.

PATENT

Attorney Docket No.: AMAT/5975.P1/CPI/COPPER/BG

Express Mail No.: EV351031212US

42. The method of claim 41, wherein the ruthenium-containing compound is selected from the group consisting of:

tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium;  
bis(2,4-dimethylpentadienyl)ruthenium;  
dicarbonyl pentadienyl ruthenium; ruthenium acetyl acetonate;  
(2,4-dimethylpentadienyl)ruthenium(cyclopentadienyl);  
bis(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium(1,5-cyclooctadiene);  
(2,4-dimethylpentadienyl)ruthenium(methylcyclopentadienyl);  
(1,5-cyclooctadiene)ruthenium(cyclopentadienyl);  
(1,5-cyclooctadiene)ruthenium(methylcyclopentadienyl);  
(1,5-cyclooctadiene)ruthenium(ethylcyclopentadienyl);  
(2,4-dimethylpentadienyl)ruthenium(ethylcyclopentadienyl);  
(2,4-dimethylpentadienyl)ruthenium(isopropylcyclopentadienyl);  
bis(N,N-dimethyl 1,3-tetramethyl diiminato)ruthenium(1,5-cyclooctadiene);  
bis(N,N-dimethyl 1,3-dimethyl diiminato)ruthenium(1,5-cyclooctadiene);  
bis(allyl)ruthenium(1,5-cyclooctadiene), ( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)ruthenium(1,3-cyclohexadiene);  
bis(1,1-dimethyl-2-aminoethoxylato)ruthenium(1,5-cyclooctadiene);  
bis(1,1-dimethyl-2-aminoethylaminato)ruthenium(1,5-cyclooctadiene);  
and combinations thereof.

43. The method of claim 42, wherein the reducing gas comprises one or more gases selected from the group consisting of hydrogen, ammonia, silane, disilane, dimethylsilane, methylsilane, ethylsilane, chlorosilane, dichlorosilane, hexachlorodisilane, borane, diborane, triborane, tetraborane, pentaborane, triethylborane, and combinations thereof.

44. The method of claim 43, wherein forming the ruthenium layer is performed at a temperature in a range from about 200°C to about 400°C.

45. The method of claim 43, wherein forming the ruthenium layer is performed at a pressure in a range from about 0.1 Torr to about 80 Torr.



PATENT

Attorney Docket No.: AMAT/5975.P1/CPI/COPPER/BG

Express Mail No.: EV351031212US

46. The method of claim 42, wherein the purge gas is selected from the group consisting of helium, argon, hydrogen, nitrogen, and combinations thereof.
47. The method of claim 45, wherein the ruthenium-containing compound is pulsed into the process chamber in a range from about 0.05 seconds to about 1.5 seconds.
48. The method of claim 47, wherein the reducing gas is pulsed into the process chamber in a range from about 0.1 seconds to about 2 seconds.
49. The method of claim 46, wherein the purge gas is pulsed into the process chamber in a range from about 0.07 seconds to about 1 second.
50. The method of claim 43, wherein the ruthenium layer has a thickness in a range from about 10 Å to about 100 Å.
51. The method of claim 43, wherein the ruthenium-containing compound passes through a gas delivery apparatus and is injected into the process chamber.
52. The method of claim 51, wherein the ruthenium-containing compound is delivered normal to the substrate with respect to the substrate.